PATENT ABSTRACTS OF JAPAN

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(54) TREATMENT OF PRINTED CIRCUIT BOARD

(57)Abstract:
PROBLEM TO BE SOLVED: To recover valuable metals such as copper without inducing environmental problem caused by eluted lead from a solder.
SOLUTION: This treating method of a printed circuit board is constituted of dipping the printed circuit board containing at least a polyester resin in an alkaline aq. solution. A metallic foil such as a copper foil is easily removed from the board by swelling the polyester resin. The swelling of the polyester resin is accelerated by dipping in water after dipping in the alkaline aq. solution to utilize the difference in osmotic pressure and further facilitates the separation and the removal of the metallic foil or parts.

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AN 1997:692142 CAPLUS
DN 127:322444
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TI Treatment of waste printed wiring boards by dipping in alkaline aqueous solution
IN Shiino, Toru; Yamagata, Yoshikazu; Terada, Takahiko; Onishi, Hiroshi; Sonoda, Nobuo
PA Matsushita Electric Industrial Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
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DT Patent
LA Japanese
IC ICM B09B005-00
ICS B29B017-00; C08J011-16
CC 60-4 (Waste Treatment and Disposal)
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PRAI	JP 1996-86724		19960409		

AB The process involves dipping of printed wiring boards contg. a polyester resin in an alk. aq. soln. and optionally dipping in water. Wiring metal foils contg. solders are easily sepd. from the boards. Valuable metals (e.g., Cu) can be **recovered** and **recycled** and Pb can be prevented from elution from solders.
ST waste printed wiring board alk dipping; copper **recovery** waste PWB alk dipping; lead elution preventing waste PWB solder
IT **Recycling**
(nonferrous metal, copper; treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT Polyesters, uses
RL: DEV (Device component use); USES (Uses)
(printed wiring boards contg.; treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT Solders
(sepn. of; treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT Printed **circuit boards**
Solid wastes
(treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT 7439-92-1, Lead, processes
RL: REM (Removal or disposal); PROC (Process)
(solders contg.; treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT **1310-58-3**, Potassium hydroxide, uses **1310-73-2**, Sodium hydroxide, uses
RL: NUU (Other use, unclassified); USES (Uses)
(treatment of waste printed wiring boards by dipping in alk. aq. soln. for copper **recovery** and suppressed lead elution)
IT 7440-50-8P, Copper, uses
RL: DEV (Device component use); PUR (Purification or recovery); PREP (Preparation); USES (Uses)

DERWENT-ACC-NO: 1998-003340

DERWENT-WEEK: 199801

TITLE: PCB treatment - comprises immersing board containing polyester resin into basic aqueous solution

PATENT-ASSIGNEE: MATSUSHITA DENKI SANGYO KK[MATU]

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ABSTRACTED-PUB-NO: JP 09271748A

BASIC-ABSTRACT:

The process comprises immersing the PCB which contains polyester resin into a basic aqueous solution. The PCB is then treated with water. The processes are repeated at least once. If single or multiple parts are installed on the PCB, the parts are removed from it and the board is treated as above. The base board of the PCB is made from paper or fabric.

USE - Used for treating waste PCB's containing polyester.

ADVANTAGE - By treating PCB's with basic aqueous solution then with water,
polyester resin is made to swell and copper foils printed on the boards are
easily removed from the base boards.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: PCB TREAT COMPRISE IMMERSE BOARD CONTAIN POLYESTER RESIN BASIC
AQUEOUS SOLUTION

DERWENT-CLASS: A23 A85 L03 P43 V04

CPI-CODES: A05-E01C; A08-S02; A12-E07A; L03-H04E9;

EPI-CODES: V04-R15;

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Polymer Index [1.2]
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K9483 ; K9552 K9483 ; Q9999 Q7818*R ; B9999 B5243*R B4740 ; K9950
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018 ; R01514 D00 D67 F21 H* O* 6A Na 1A ; R01740 G2335 D00 F20 H*
O* 6A ; A999 A475

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CPI Secondary Accession Numbers: C1998-001334
Non-CPI Secondary Accession Numbers: N1998-002434

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of processing the printed circuit board which contains polyester resin at least.
[0002]
[Description of the Prior Art] As printed circuit boards, such as a common noncommercial electrical machinery and apparatus, the paper base polyester resin laminate and the cloth base material polyester resin laminate are used widely. At the time of product abandonment, after dissociating from a product together with a product, as for these substrates, it is common to crush, or to reclaim land and process in soil as it is.
[0003]
[Problem(s) to be Solved by the Invention] Many copper clad laminates to which copper wiring was given are used for printed circuit boards, such as a paper base polyester resin laminate and a cloth base material polyester resin laminate, and IC chip, a capacitor, resistance, switches, and connectors are mainly mounted in them using solder. If it crushes and reclaims land from such a printed circuit board and it is processed with the condition, an environmental problem -- lead is eluted -- will arise from solder. Moreover, since recovery of valuable metals, such as copper, is not performed, either, it has been a problem also from the point of a deployment of a resource. However, only by such a printed circuit board carrying out crushing processing simply, a metal and resin cannot fully be separated but recycle is difficult. Then, this invention aims to let the processing at the time of abandonment offer the art of an easy printed circuit board.
[0004]
[Means for Solving the Problem] The art of the printed circuit board of this invention is characterized by immersing the printed circuit board which contains polyester resin at least in an alkaline water solution. Moreover, immersion down stream processing that the printed circuit board which contains polyester resin at least is immersed in water after being immersed in an alkaline water solution is performed once [at least] or more. Moreover, about the printed circuit board containing the polyester resin with which an unit or two or more components are mounted in the metal wiring section, after removing said

some of components [at least], it is immersed in an alkaline water solution and said metal wiring section is exfoliated. As for a printed circuit board, it is desirable that they are a paper base or a cloth base material.

[0005]

[Embodiment of the Invention] If the printed circuit board with which this invention is presented is a printed circuit board containing polyester resin, any will be sufficient, for example, a paper base polyester resin laminate, a cloth base material polyester resin laminate, a glass fabric base material polyester resin laminate, an asbestos base material polyester resin laminate, a synthetic-fiber base material polyester resin laminate, etc. will be mentioned. Of course, components, such as IC chip, a capacitor, resistance, switches, and connectors, may be mounted in these printed circuit boards, and resists, adhesive tape, etc., such as a photoresist and a screen-stencil mold resist, may be attached to them. Furthermore, coating of these printed circuit boards may be carried out with the coating material which tends to be invaded by alkali. As a coating material which tends to be invaded by this alkali, polyurethane, silicone, acrylic resin, isobutylene isoprene rubber, etc. are mentioned, for example.

[0006] Moreover, most may use conductive metallic foils, such as silver, aluminum, and nickel, for wiring of a printed circuit board besides it, although copper foil is used. Moreover, the adhesives currently generally used may be used, as thermosetting resin, there are phenol resin, an epoxy resin, REJIRUSHI Norian resin, etc., and there are a polyvinyl butyral, nitrile rubber, etc. in the adhesives which are making these metallic foils and substrates rival as thermoplastics, for example. Polyvinyl-butyral denaturation phenol resin, acrylic nitrile rubber denaturation phenol resin, a modified epoxy resin, etc. are still more specifically mentioned.

[0007] The alkaline water solution with which this invention is presented is a water solution containing an alkaline alkali metal compound or an alkaline alkaline-earth-metal compound. As an alkaline alkali metal compound or an alkaline alkaline-earth-metal compound, a sodium hydroxide, a potassium hydroxide, a barium hydroxide, a sodium ethoxide, potassium butoxide, etc. are mentioned, for example. The concentration of the solution of these alkaline alkali metal compounds or an alkaline alkaline earth metal compound invades the adhesives which are making polyester resin, a resist and the metallic foil for wiring, and the substrate rival, so that it is high. However, since sodium ion, potassium ion, etc. increase in number, the viscosity of a solution also becomes high, and the permeability of the liquid to the inside of a printed circuit board falls. Therefore, concentration to which resin etc. is invaded enough and the permeability of liquid is not reduced, either is desirable. Then, the solution concentration of an alkaline alkali metal compound or an alkaline alkaline-earth-metal compound has desirable 10Ns or less, and 0.5-especially 7N are 1-5N more desirable still more preferably. In addition, two or more these alkaline alkali metal compounds or alkaline alkaline-earth-metal compounds may be contained only not only in the single component.

[0008] Moreover, in order to improve the permeability over the printed circuit board of a solution For example, alcohols, such as methyl alcohol and ethyl alcohol, Furans, such as ketones, such as an acetone and a methyl ethyl ketone, and a tetrahydrofuran Ethylene

glycol, a diethylene glycol, propylene glycol, Glycols, such as dipropylene glycol, ethylene glycol monomethyl ether, Ethylene glycol wood ether, ethylene glycol monoethyl ether, Ethylene glycol diethylether, ethylene glycol mono-isopropyl ether, The ethylene glycol monopropyl ether, the ethylene glycol mono-isobutyl ether, Ethylene glycol monoalkyl ether or ethylene glycol dialkyl ether, such as ethylene glycol monobutyl ether and the ethylene glycol mono-isopentyl ether, The diethylene-glycol monomethyl ether, diethylene-glycol wood ether, Diethylene glycol monoethyl ether, diethylene-glycol diethylether, Diethylene-glycol mono-isopropyl ether, the diethylene-glycol monopropyl ether, The diethylene-glycol mono-isobutyl ether, the diethylene-glycol monobutyl ether, Diethylene-glycol monoalkyl ether or diethylene-glycol dialkyl ether, such as the diethylene-glycol mono-isopentyl ether, The triethylene glycol monomethyl ether, triethylene glycol wood ether, The triethylene glycol monoethyl ether, triethylene glycol diethylether, Triethylene glycol monoalkyl ether or triethylene glycol dialkyl ether, such as triethylene glycol mono-isopropyl ether and the triethylene glycol monopropyl ether, Propylene glycol monomethyl ether, propylene glycol wood ether, Propylene glycol monoalkyl ether or propylene glycol dialkyl ether, such as the propylene glycol monoethyl ether and propylene glycol diethylether, Dipropylene glycol monomethyl ether, dipropylene glycol wood ether, Dipropylene glycol monoalkyl ether or dipropylene glycol dialkyl ether, such as the dipropylene glycol monoethyl ether and dipropylene glycol diethylether, Dimethylformamide, dimethylamine, a cation, an anion, and the various surfactants of a non-ion system may be added.

[0009] Moreover, it is more desirable to warm processing temperature by within the limits below the boiling point of water (ordinary pressure 100 degrees C or less), since an osmosis rate with the bigger elevated temperature is obtained. When alcohols are contained, below those boiling points are desirable. When immersed in water after alkaline water-solution immersion, the highest possible temperature of the temperature of the water is also better at below the boiling point. In the art immersed in the alkaline water solution of this invention, polyester resin, a resist and the metallic foil for wiring, the adhesives of a substrate, coating, etc. are invaded by alkali, and decomposition, the dissolution, swelling, etc. occur. Therefore, swelling of a printed circuit board, softening, exfoliation of a laminate, exfoliation of the metallic foil for wiring, exfoliation of coating, etc. are promoted, and it becomes possible to separate a printed circuit board and the metallic foil for wiring easily. By this, the components mounted in the printed circuit board can also be easily removed now, and mounting components, the metallic foil for wiring, and a polyester resin substrate can be separated. Since each separated thing can be processed separately respectively, it becomes suitable processing and playback, and reusable. Since most especially solder has adhered to the metallic foil, by processing appropriately, the load to an environment can be made small and recycle of metallic foils, such as copper, is also attained.

[0010] moreover, in the art which performs immersion down stream processing of being immersed in water, once [at least] or more after being immersed in the alkaline water solution of this invention In the condition of having made the alkaline water solution permeating into a printed circuit board, by being immersed in water Make the liquid of the

interior of a printed circuit board, and the exterior produce osmotic pressure difference, tend to cancel the osmotic pressure difference, and a lot of water infiltrates into the interior of a printed circuit board. It enables them to promote further swelling of a printed circuit board, softening, exfoliation of a laminate, etc., and to carry out exfoliation removal of the metallic foil for wiring from a printed circuit board more easily. in addition, the temperature of said water -- below the boiling point -- it is -- ****ing -- warming -- if it is a condition, since permeability increases more, it is desirable. Moreover, since the degree of hardness is falling greatly, the polyester resin substrate after processing can be ground easily, and can create a pulverizing article by low energy. In this grinding, the polyester resin substrate of a condition [having become wet after processing] is put into impact type pulverizers, such as grinding type grinders, such as a grinder, and a hammer mill, a ball mill, a mixer, etc., and it can grind easily. Moreover, in order to avoid the coagulation at the time of desiccation of a pulverizing article etc., use of a spray type dryer is desirable. Thus, the created pulverizing article is reusable to a filler etc. Moreover, the separated metal can carry out separation recovery of solder and the copper by melting processing.

[0011]

[Example] Hereafter, a concrete example is given and this invention is explained more to a detail.

<<example 1>> In this example, the paper base polyester resin laminate, the cloth base material polyester resin laminate, and the glass base material polyester resin laminate were used as a printed circuit board. All of size are 1.5mm in the magnitude of 30x30mm, and thickness. Polyvinyl-butyral denaturation phenol resin (mixture of a polyvinyl butyral (trade name S lek B by Sekisui Chemical Co., Ltd.) and phenol resin) is used for one side of these substrates, copper foil with a thickness of 35 micrometers was pasted up on it, the Kushigata electrode of 0.3mm pitch was created, and eutectic solder was made to adhere to several of the places. Immersion processing of these three kinds of printed circuit boards was carried out at 80 degrees C for 20 hours at the 5-N sodium-hydroxide water solution. The thickness of the substrate before and behind immersion processing and weight were measured. The thickness rate of change and weight rate of change of a substrate after the immersion processing to the substrate before immersion processing are shown in Table 1.

[0012]

[Table 1]

	紙基材ﾌｪﾉｰﾙﾎﾟﾘｴｽﾃﾙ	布基材ﾌｪﾉｰﾙﾎﾟﾘｴｽﾃﾙ	ガラス基材ﾌｪﾉｰﾙﾎﾟﾘｴｽﾃﾙ
厚み変化率	＋２５１％	＋２４３％	＋１５０％
重量変化率	＋１０５％	＋８５％	＋３５％

[0013] From this result, it saw, and the increment swelled thickness and weight and deformed them for every substrate for a while. Moreover, since a part of copper foil exfoliated, and every substrate was turned over and went up, when the pincette pulled that, while [which exfoliates copper foil easily] things could be carried out and solder had also adhered to copper foil, it has removed. Especially, compared with the glass base material polyester resin laminate, exfoliation of copper foil and removal of a paper base polyester resin laminate or a cloth base material polyester resin laminate were completed more

easily. A printed circuit board is easily separable into a laminate and a conductive metallic foil with this.

[0014] Next, immersion processing of the same printed circuit board as the above was carried out at 80 degrees C for 20 hours at the 5-N potassium-hydroxide water solution. The thickness of the substrate before and behind immersion processing and weight were measured. The thickness rate of change and weight rate of change of a substrate after the immersion processing to the substrate before immersion processing are shown in Table 2.

[0015]

[Table 2]

	紙基材ポリエステル	布基材ポリエステル	ガラス基材ポリエステル
厚み変化率	+249%	+245%	+135%
重量変化率	+103%	+87%	+34%

[0016] From this result, also when a potassium-hydroxide water solution was used, it was shown that the same effectiveness as the case where the above-mentioned sodium hydroxide is used is acquired.

[0017] Immersion processing of the same paper base printed circuit board as the above was carried out at 80 degrees C for 20 hours at the sodium-hydroxide water solution (0.1N, 0.5N, 1N, 3N, 5N, 7N, and 10N). The thickness rate of change of the substrate after the immersion processing to the substrate before immersion processing was measured. The result is shown in Table 3.

[0018]

[Table 3]

濃度	0.1N	0.5N	1N	3N	5N	7N	10N
判定結果	×	○	◎	◎	◎	○	△

[0019] The criterion in Table 3 is as follows.

O Less than [220% / of :thickness rate of change / or more O:rate-of-change / thickness / 200% or more / less than 220% / **:thickness rate of change / 200% / 150% or more] x : it is more desirable more less than 150% of thickness rate of change consequently and to use 0.5-N or more alkali water solution 7Ns or less, and 1 moreNs or more 5Ns or less are the most desirable.

[0020] <<example 2>> In this example, suitable wiring was created by the copper foil used for the example 1 to the paper base polyester resin laminate with a magnitude [of 50x50mm], and a thickness of 1.5mm, and the printed circuit board which mounted one IC chip, ten resistance, three capacitors, and one connector with soldering at one side of a substrate was created. Immersion processing of this printed circuit board was carried out at 80 degrees C for 20 hours at the 5-N sodium-hydroxide water solution. Consequently, the printed circuit board swelled, the resist separated completely, and some laminates exfoliated. Moreover, when the part into which a part of copper foil exfoliated was seen and the pincette pulled the exfoliation part, copper foil has exfoliated with solder. Therefore, when the pincette pulled the mounted components, it could remove easily and has separated into the copper foil to which a laminate, components, and solder adhered. Thus, by processing the printed circuit board which mounted components by the art of this

invention, it becomes recoverable [metals, such as removal of components and copper foil,] easily.

[0021] <<example 3>> In this example, the same component-mounting printed circuit board as an example 2 was processed as follows. first, the wire part of the resistance and the capacitor which are connected by the wire among mounting components and connection of IC chip and a connector -- the foot was cut and separation removal of the components was carried out from the printed circuit board. Then, immersion processing of the substrate from which components were removed was carried out at 80 degrees C for 20 hours at the 5-N sodium-hydroxide water solution. Consequently, the printed circuit board swelled, the resist separated completely, and some laminates exfoliated. Moreover, since a part of copper foil exfoliated, when the field was rubbed with the polypropylene brush, the exfoliation removal of the wire part and foot of copper foil, solder, and components could be carried out together, and it has separated into the metal sections, such as a polyester resin substrate and copper foil. Thus, before processing in an alkaline water solution, a next exfoliation process can be made easy by removing mounting components beforehand.

[0022] <<example 4>> In this example, after carrying out immersion processing of these at 80 degrees C for 15 hours at a 5-N sodium-hydroxide water solution using three kinds of the same printed circuit boards as an example 1, it was immersed in 80-degree C water, and processed for 3 hours. The thickness of the substrate after each immersion processing and weight were measured. The thickness rate of change and weight rate of change of a substrate after the immersion processing to the substrate before immersion processing are shown in Table 4.

[0023]

[Table 4]

		紙基材ポリエステル	布基材ポリエステル	ガラス基材ポリエステル
厚み変化率	TMAH処理後	+215%	+198%	+115%
	水処理後	+282%	+261%	+185%
重量変化率	TMAH処理後	+85%	+50%	+30%
	水処理後	+135%	+104%	+75%

[0024] By comparing this result with the result of an example 1 shows carrying out that swelling [carry out / move to water and / after alkaline water-solution immersion processing, / immersion processing] is bigger, and the increment in weight rather than carrying out long duration immersion processing in an alkaline water solution. By big change of such a substrate, the part into which copper foil exfoliated also increased and separation of copper foil became easier. Every substrate has separated copper foil easily using the pincette.

[0025] <<example 5>> In this example, after being immersed in the 5-N sodium-hydroxide water solution at 80 degrees C for 15 hours using the same component-mounting printed circuit board as an example 2, it moved to 80-degree C water, and immersion processing was carried out for 3 hours. Consequently, the printed circuit board swelled, the resist separated completely, and some laminates exfoliated. Moreover, only in exfoliation, the

beam part was seen and copper foil has exfoliated [a part of copper foil] with solder easily from the exfoliation part. Therefore, the mounted components could also be removed easily and it has separated into the copper foil to which a laminate, components, and solder adhered. In addition, the ease of exfoliating of copper foil is easier than an example 2, and has been processed more in a short time.

[0026] <<example 6>> In this example, separation removal of the mounting components was first carried out for the same component-mounting printed circuit board as an example 2 from the printed circuit board like the example 3. Then, after carrying out immersion processing of the substrate from which components were removed at 80 degrees C for 15 hours at a 5-N sodium-hydroxide water solution, it moved to 80-degree C water, and immersion processing was carried out for 3 hours. Consequently, the printed circuit board swelled, the resist separated completely, and some laminates exfoliated. Moreover, when a part of copper foil rubbed the field only for exfoliation with the polypropylene brush for the beam reason, the exfoliation removal of the wire part and foot of copper foil, solder, and components could be carried out together, and they have separated into the metal sections, such as a polyester resin substrate and copper foil. Since there were more exfoliation parts than an example 3, this exfoliation removal was more easy.

[0027] <<example 7>> The coating material (trade name: HYUMI seal (BOKUSUI Brown, Inc.)) of an urethane system covered the front face for the same component-mounting printed circuit board as an example 2 in this example. This printed circuit board was moved to 80-degree C water, after being immersed in the 5-N sodium-hydroxide water solution at 80 degrees C for 20 hours, and immersion processing was carried out for 3 hours. Consequently, the coating material exfoliated, while carrying out immersion processing at the alkaline water solution, and swelling of a printed circuit board, exfoliation of a resist, exfoliation of some laminates, etc. were seen. Moreover, only in exfoliation, the beam part was seen and copper foil has exfoliated [a part of copper foil] with solder easily from the exfoliation part. Therefore, the mounted components could also be removed easily and it has separated into the copper foil to which a laminate, components, and solder adhered. Thus, it was able to process similarly by the printed circuit board which performed coating.

[0028] In addition, in the above example, although the sodium-hydroxide water solution was used as an alkaline water solution, it is not limited to this and a potassium-hydroxide water solution, a sodium-ethoxide water solution, etc. which were mentioned above may be used. Moreover, although it had put on an alkaline water solution or water gently in the above example while carrying out immersion processing of the printed circuit board, a resist, exfoliation removal of coating, etc. may be performed, agitating or covering [are not limited to this approach,] a brush in liquid. Furthermore, a supersonic wave and a pressure are put, the permeability of liquid can be raised or removal of mounting components etc. can be promoted. Moreover, in the case of the printed circuit board in which components were mounted, approaches, such as carrying out melting of the solder, may be used as an approach of removing mounting components beforehand, before processing by the alkaline water solution, applying heat. Furthermore, when not removing components, applying heat beforehand when components process the printed circuit board

by which surface mounting is carried out, since components are removed from a printed circuit board together with a metallic foil, they can be divided into a printed circuit board and the metallic foil to which components adhered.

[0029]

[Effect of the Invention] If this invention is caused as mentioned above, by carrying out immersion processing of the printed circuit board which contains polyester resin at least at an alkaline water solution, polyester resin can be made to be able to swell, it can change into the condition of being easy to exfoliate copper foil from a substrate, and these separation can be made easy. Moreover, after being immersed in an alkaline water solution, by being immersed in water, the swelling of polyester resin is promoted using osmotic pressure difference, and the separation removal of copper foil or the components can be carried out more easily. According to the art of this invention, there is also no generating of noise, such as the conventional crushing processing, metallic foils can be easily collected from a substrate, and the reuse can also be performed.

[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The art of the printed circuit board characterized by having the process immersed in an alkaline water solution in the printed circuit board which contains polyester resin at least.
[Claim 2] The art of the printed circuit board characterized by performing immersion down stream processing immersed in water in the printed circuit board which contains polyester resin at least after being immersed in an alkaline water solution once [at least] or more.
[Claim 3] The art of the printed circuit board characterized by immersing the printed circuit board containing the polyester resin with which an unit or two or more components are mounted in the metal wiring section in an alkaline water solution after removing said some of components [at least], and exfoliating said metal wiring section.
[Claim 4] The art of the printed circuit board according to claim 1 to 3 which said printed circuit board turns into from paper or a cloth base material.

[Translation done.]